Highly electron-deficient neutral and cationic zirconium complexes with bis(sigma-aryl)amine dianionic tridentate ligands

Bouwkamp, M.W.; van Leusen, D.; Meetsma, A.; Hessen, B.

Published in:
Organometallics

DOI:
10.1021/om980358s

Publication date:
1998

Supporting Material to:

"Highly Electron-Deficient Neutral and Cationic Zirconium Complexes with bis(σ-aryl)-amine Dianionic Tridentate Ligands "

by M. Bouwkamp, D. van Leusen, A. Meetsma, and B. Hessen

Part I: Experimental Section

General

All experiments were performed under nitrogen atmosphere using standard glove-box, Schlenk, and vacuum line techniques, except where mentioned otherwise. Deuterated solvents (Aldrich) were either dried over Na/K alloy and vacuum transferred before use (C_6D_6) or flushed with nitrogen and stored over mol. sieves (C_6D_5Br). Diethyl ether, THF, toluene and pentane were distilled from Na or Na/K alloy before use. $B(C_5F_5)_3$ was prepared according to literature procedures (Massey, A. G.; Park, A. *J. Organomet. Chem.* **1964**, *2*, 245), $[Ph_3C][B(C_6F_5)_4]$ was used as obtained from AKZO Nobel. $Zr(CH_2Ph)_2Cl_2(OEt_2)_2$ was prepared according to Wengrovius, J. H.; Schrock, R. R. *J. Organomet. Chem.* **1981**, *205*, 319, 2-bromo-3-methylbenzylbromide according to Miyano *et al. Bull. Chem. Soc. Jpn.* **1986**, *59*, 3285, and 1-bromo-2-naphtylmethylbromide according to Newman & Kosak, *J. Org. Chem.* **1949**, *14*, 375. Ethene and propene (AGA 99.5%) were passed over a supported copper scavenger (BASF R 3-11) and mol. sieves (3Å) before being passed to the reactor. NMR spectra were run on Varian Gemini 200, VXR-300 and Unity-500 spectrometers. Elemental analyses were performed by the Microanalytical Department of the University of Groningen. Every value is the average of at least two independent determinations.

Di-(2-bromo-3-methylbenzyl)methylamine. *(performed under aerobic conditions)* In 50 mL of DMSO, 2-bromo-3-methylbenzylbromide (13.6 g, 51.5 mmol), methylamine hydrochloride (1.69 g, 25 mmol) and K_2CO_3 (10.5 g, 75 mmol) were heated ar 80°C for 5 h with stirring. The mixture was poured into water (500 mL). After extraction with petroleum ether (bp 40-60°C, 100, 50 and 50 mL), the combined extracts were washed with brine, dried over Na_2SO_4 and concentrated. Short-path distillation (bath temperature 130-170°C, 0.04 mm Hg) gave 9.0 g (22.7 mmol, 90%) of the title compound.

^{1}H NMR ($CDCl_3$, 25°C): δ 2.31 (s, 3H, NMe), 2.46 (s, 6H, Ar Me), 3.78 (s, 4H, NCH_2), 7.13-7.25 (m, 4H, Ar H), 7.43-7.48 (m, 2H, Ar H). ^{13}C(APT) NMR ($CDCl_3$, 25°C): δ 138.7, 138.3 (Ar C), 129.1, 129.9 (Ar CH), 127.0 (Ar C)Br, 126.6 (Ar CH), 61.9 (NCH_2), 42.2 (NMe), 23.6 (Ar Me).

Exact EI-MS (m/e): 396.9846 (75%, M^+ , calcd 396.9864), 316.1 (10%, $[M-Br]^+$), 226.0 (100%), 212.0(50%), 183.0 (95%).

Di-(2-lithio-3-methylbenzyl)methylamine (1a). To a stirred solution of di-(2-bromo-3-methylbenzyl)methylamine (3.61 g, 9.1 mmol) in 30 mL of diethyl ether was slowly added a 2.5 N solution of *n*BuLi in hexane (8.0 mL) at -30°C. The mixture was warmed to ambient temperature and stirred for 0.5 h. After addition of 25 mL of hexane the mixture was concentrated to a volume of ca 30 mL, and this was repeated several times. Subsequently all volatiles were pumped off, the residue was rinsed with pentane and dried *in vacuo* to give 2.54 g (3.6 mmol, quantitative yield) of **1a**.0.33 Et_2O.

^{1}H-NMR (C_6D_6/d_8-THF, 25°C): δ 1.02 (t, J = 7 Hz, OCH_2CH_3), 2.20 (s, 3H, NMe), 2.60 (s, 6H, Ar Me), 3.20 (q, J = 7 Hz, OCH_2CH_3), 3.37 and 4.00 (d, J = 14 Hz, 2H each, NCH_2), 6.83-7.12 (m, 6H, Ar H) (Et_2O resonances omitted. Their intensity corresponds with the composition **1a**.0.33 Et_2O)

Di-(1-bromo-2-naphtylmethyl)methylamine. *(performed under aerobic conditions)* A mixture of 1-bromo-2-naphtylmethylbromide (10.0 g, 33.3 mmol), methylamine hydrochloride (1.13 g, 16.7 mmol) and K_2CO_3 (6.7 g, 48.5 mmol) in 25 mL of DMSO was stirred for 5 h at 90°C. The mixture was poured into water (150 mL), the precipitated solid was collected and rinsed with 25 mL of methanol. Recrystallization from 200 mL of acetonitrile gave 5.95 g (76%) of the title compound. Mp 86-98°C, Anal. calcd (%) for $C_{23}H_{19}Br_2N$ (469.22): C, 58.87; H, 4.08; N, 2.99; Br, 34.06. Found: C, 58.81; H, 4.13; N, 3.10; Br, 34.10.

^{1}H NMR ($CDCl_3$, 25°C): δ 2.34 (s, 3H, NMe), 4.03 (s, 4H, NCH_2), 7.47-7.85 (m, 10H, Ar H), 8.37 (d, J = 10 Hz, 2H, Ar H). ^{13}C(APT) NMR ($CDCl_3$, 25°C): δ 136.6, 132.3 (Ar C), 128.0, 127.4, 127.3, 127.2, 126.2 (Ar CH), 124.2 (Ar CBr), 62.0 (NCH_2), 42.2 (NMe).

Di-(1-lithio-2-naphtylmethyl)methylamine (1b). To a suspension of di-(1-bromo-2-naphtylmethyl)methylamine (2.34 g, 5.0 mmol) in 25 mL of diethyl ether was added a 2.5 N solution of *n*BuLi in hexane (4.0 mL) at 0°C. The mixture was warmed to ambient temperature and stirred for 0.5 h. After addition of 15 mL of hexane hexane the mixture was concentrated to a volume of ca 10 mL, and this was repeated several times. The mixture was decanted and the solid rinsed with pentane and dried *in vacuo* to give 1.74 g (97%) of **1b**.0.5 Et_2O.

^{1}H-NMR (C_6D_6/d_8-THF, 25°C): δ 1.05 (t, J = 7 Hz, 3H, OCH_2CH_3), 2.33 (s, 3H, NMe), 3.21 (q, J = 7 Hz, 2H, OCH_2CH_3), 3.65 and 4.38 (d, J = 14 Hz, 2H each, NCH_2), 7.29-7.64 (m, 6H, Ar H), 7.72 (d, J = 8 Hz, 2H, Ar H), 7.88 (d, J = 8 Hz, 2H, Ar H), 8.28 (d, J = 8 Hz, 2H, Ar H).

[(*o*-Me-$C_6H_3CH_2)_2$NMe]$_2$Zr (2). Solid **1a**.0.33Et_2O (0.368 g, 1.33 mmol) was added to a suspension of $ZrCl_4$ (0.153 g, 0.66 mmol) in 7.5 mL of toluene an ambient temperature. After 1 h, 15 mL of pentane was added and the fine precipitate was allowed to settle over a period of 4 days. The mixture was filtered and the volatiles were removed *in vacuo*. The residue was recrystallized by slow vapor diffusion of 10 mL of pentane into a solution in 2 mL of toluene to give 0.123 g (33%) of **2** as colorless crystals suitable for single crystal X-ray diffraction.
^{1}H NMR (C_6D_6, 25°C): δ 1.97 (s, Me), 2.28 (s, Me), 2.37 (s, Me), 2.64 and 5.03 (d, $^2J_{HH}$ = 14 Hz, NCH_2), 2.90 and 3.99 (d, $^2J_{HH}$ = 14 Hz, NCH_2), 6.78, 6.83, 6.94, 6.99 (all d, $^2J_{HH}$ = 7.3-7.6 Hz, Ar H), 7.10 (t, Ar H, other signal overlapped by solvent). $^{13}C\{^1H\}$ NMR (C_6D_6, 25°C): δ 26.11 and 26.30 (Ar Me), 48.04 (NMe), 61.54 and 64.90 (NCH_2), 122.38, 123.06, 126.98, 127.22 (Ar CH, other two resonances overlapped by solvent), 144.48, 144.64, 145.27, 146.14 (Ar C-C), 195.05, 195.87 (Ar C-Zr).

[($C_{10}H_6CH_2)_2$NMe]Zr($CH_2Ph)_2$ (3). A solution of **1b**.0.5 Et_2O (0.596 g, 1.6 mmol) in 50 mL of ether was added to a stirred solution of Zr($CH_2Ph)_2Cl_2$.Et_2O (0.697 g, 1.6 mmol) in 70 mL of diethyl ether at 0°C. After 30 min. the solution was warmed to ambient temperature and stirring was continued for 30 min. The solvent was pumped off, 20 mL of pentane was added and, after stirring, pumped off again (to remove residual ether). Subsequently the residue was extracted with diethyl ether. Recrystallizing the extract from diethyl ether by cooling to -30°C resulted in 0.279 g (30%) of **3** as yellow crystals suitable for elemental analysis and single crystal X-ray diffraction.
Anal. calcd (%) for $C_{37}H_{33}NZr$ (582.90): C, 76.24; H, 5.71; Zr, 15.65. Found: C, 76.00; H, 5.77; Zr, 15.72.
^{1}H NMR (C_6D_6, 25°C): δ 1.88 (s, NMe), 3.21 (s, $ZrCH_2$), 3.55 (s, $ZrCH_2$), 3.29 and 3.86 (d, $^2J_{HH}$ = 14.3 Hz, NCH_2), 6.18 (d, $^3J_{HH}$ = 7.0 Hz, Bz *o*-H), 6.4-6.5 (m, Bz *m*-H and *p*-H), 6.61 (d, $^3J_{HH}$ = 6.3 Hz, Bz *o*-H), 6.98 (d, $^3J_{HH}$ = 8.0 Hz, Ar H), 7.44 (t, $^3J_{HH}$ = 7.5 Hz, Ar H), 7.43 (t, Ar H), 7.45 (d, Ar H), 7.85 (d, $^3J_{HH}$ = 8.0 Hz, Ar H), 9.13 (d, $^3J_{HH}$ = 8.1 Hz, Ar H); assignments were aided by recording a ^{1}H,^{1}H COSY NMR spectrum. ^{13}C NMR (C_6D_6, 25°C): δ 43.43 (q, J_{CH} = 147.8 Hz, NMe), 71.51 (t, J_{CH} = 136.7 Hz, NCH_2), 82.23 (t, J_{CH} = 131.9 Hz, $ZrCH_2$), 85.45 (t, J_{CH} = 119.6 Hz, $ZrCH_2$), 121.59, 122.35, 123.36, 125.14, 126.17, 127.43, 128.41, 128.47, 129.52, 129.80, 129.83, 131.06 (all d, Ar CH), 132.65, 136.59, 141.11, 143.94, 146.48 (all s, Ar C), 192.07 (s, Ar C-Zr).

Generation of [($C_{10}H_6CH_2)_2$NMe]Zr(CH_2Ph)[Ph$CH_2B(C_6F_5)_3$] (5). A solution of $B(C_6F_5)_3$ (13.9 mg, 27 μmol) in 0.35 ml of C_6D_5Br was added to a solution of **3** (15.5 mg, 27 μmol) in

0.35 ml of C_6D_5Br. The solution rapidly turned orange. NMR spectroscopy showed clean formation of **5**.

^1H NMR (C_6D_5Br, 25°C): δ 2.11 (s, NMe), 2.88 (br, BCH_2), 3.05 (s, $ZrCH_2$), 3.46 and 4.05 (d, $^2J_{HH}$ = 14.4 Hz, NCH_2), 6.13 (t, *J* = 7.6 Hz, 3H, BBz *m*-H), 6.43 (t, *J* = 7.3 Hz, 1H, BBz *p*-H), 6.51 (d, *J* = 7.8 Hz, BBz *o*-H), 6.85 (t, *J* = 7.3 Hz, 2H, ZrBz *m*-H), 6.96 (t, *J* = 7.3 Hz, 1H, ZrBz *p*-H), 7.03 (d, *J* = 7.3 Hz, 2H, ZrBz *o*-H), 7.12 (d, *J* = 8.3 Hz, 2H, Ar H), 7.42 (ps.t, 7.3 Hz, 2H, Ar H), 7.68 (m, 4H, Ar H), 7.83 (d, *J* = 7.8 Hz, 2H, Ar H), 8.00 (d, *J* = 8.3 Hz, 2H, Ar H); assignments were aided by recording a $^1H,^1H$ COSY NMR spectrum. ^{13}C NMR (C_6D_5Br, 25°C): δ 30 (br, BCH_2), 47.65 (q, J_{CH} = 138.0 Hz, NMe), 72.05 (t, J_{CH} = 138.0 Hz, NCH_2), 92.93 (t, J_{CH} = 127.2 Hz, $ZrCH_2$), 124.55 (Ar CH), 128.58 (Ar CH), 131.80 (Ar CH), 132.76 (Ar C), 133.18 (Ar CH), 135.36 (Ar C), 139.98 (Ar C), 146.89 (Ar C), 160.85 (s, BBz Ar C), 190.94 (s, Ar C-Zr); extensive overlap with solvent resonances in the region 126-131 ppm, C_6F_5-resonances omitted. ^{19}F NMR (C_6D_5Br, 25°C): δ -132.82 (d, $^3J_{FF}$ = 21 Hz, *o*-F), -162.31 (t, $^3J_{FF}$ = 21 Hz, *p*-F), -166.72 (t, $^3J_{FF}$ = 21 Hz, *m*-F), $\Delta\delta(p\text{-}m)$ = 4.41 ppm.

Generation of {[$(C_{10}H_6CH_2)_2$NMe]Zr(CH_2Ph)}[$B(C_6F_5)_4$] (6). A solution of [Ph_3C][$B(C_6F_5)_4$] (8.7 mg, 9 μmol) in 0.35 ml of C_6D_5Br was added to a solution of **3** (5.4 mg, 9 μmol) in 0.35 ml of C_6D_5Br. The solution rapidly turned orange. NMR spectroscopy showed formation of **6** and Ph_3CCH_2Ph.

^1H NMR (C_6D_5Br, 25°C): δ 2.66 (s, NMe), 2.98 (s, $ZrCH_2$), 3.71 (s, 2H, Ph_3CCH_2Ph), 3.99 and 4.51 (d, $^2J_{HH}$ = 15.8 Hz, NCH_2), 6.47 (d, *J* = 6.4 Hz, 2H, Ar H), 6.51 (d, *J* = 7.0 Hz, 2H, Ar H), all other Ar H 6.8-7.6 ppm. ^{13}C NMR (C_6D_5Br, 25°C): δ 40.20 (q, J_{CH} = 141.6 Hz, NMe), 65.34 (t, J_{CH} = 140.4 Hz, NCH_2), 90.65 (t, J_{CH} = 141.6 Hz, $ZrCH_2$), 121.56 (s, ZrBz C), 198.85 (s, Ar C-Zr); extensive overlap with solvent resonances in the region 126-131 ppm, C_6F_5-resonances omitted.

Propene polymerization with 6. A solution of **3** (34.2 mg, 58.7 μmol) and [Ph_3C][$B(C_6F_5)_4$] (54.1mg, 58.7 μmol) in 20 mL of bromobenzene was placed in a 100 mL Büchi glass autoclave with a teflon coated stirbar. The stirred solution in the reactor was pressurized with 4 bar of propene (which was continuously supplied) at ambient temperature. After 30 min. the polymerization was terminated by venting the reactor and the subsequent addition of methanol. The reactor contents were poured into 200 mL of stirred methanol. The precipitated polymer was washed repeatedly with methanol, and dissolved in chloroform. After filtration the solvent was removed on a rotary evaporator. The resultant viscous polymer was subsequently dried *in vacuo* at 100°C for 1h. Yield: 0.760 g. Productivity: 26 kg(PP) mol(Zr)$^{-1}$ h^{-1}. NMR spectra showed that the polymer is predominantly atactic.

Supporting Material to:

"Highly Electron-Deficient Neutral and Cationic Zirconium Complexes with bis(σ-aryl)-amine Dianionic Tridentate Ligands "

by M. Bouwkamp, D. van Leusen, A. Meetsma, and B. Hessen

Part II: Structure of $[o\text{-}MeC_6H_3)_2NMe]_2Zr$ (2)

Abstract. "IUPAC-name", $(C_{17}H_{19}N)_2Zr$, M = 565.92, monoclinic, *P2/n*, *a* = 8.718(1), *b* = 9.278(1), *c* = 17.567(3) Å, β = 100.12(2)°, *V* = 1398.8(3) Å^3 *Z* = 2, D_x = 1.344 g cm^{-3}, λ(MoK$\bar{\alpha}$) 0.71073 Å, μ = 4.2 cm^{-1}, *F*(000) = 592, T = 130 K, $wR(F^2)$ = 0.0667 for 3375 reflections with $F_o^2 \geq 0$ and 244 parameters and $R(F)$ = 0.0243 for 3204 reflections obeying $F_o \geq 4.0\ \sigma(F_o)$ criterion of observability.

The asymmetric unit consists of one half molecule of the title compound with the Zr position at a twofold axis.

Experimental

X-ray diffraction: Crystal and Molecular Structure.

Suitable transparent colorless block-shaped crystals were obtained by recrystallisation from toluene/pentane. The crystal, a parallelepiped of approximate size 0.45 x 0.50 x 0.52 mm., used for characterization and data collection was mounted on top of a glass fiber by using inert-atmosphere handling techniques and was transferred into the cold nitrogen cold stream of the low temperature unit[1] mounted on an Enraf-Nonius *CAD-4F*[2] diffractometer, interfaced to a *INDY* (*Silicon Graphics*) *UNIX* computer (Mo tube, 50 kV, 40 mA, monochromated Mo-K$\bar{\alpha}$ radiation, $\Delta\omega = 0.95 + 0.34\ \mathrm{tg}\ \theta$).

Unit cell parameters[3] and orientation matrix were determined from a least-squares treatment of the *SET4*[4] setting angles of 22 reflections in the range 18.28° < θ < 20.44°. The unit cell was identified as monoclinic; reduced cell calculations did not indicate any higher metric lattice

symmetry.[5] Systematic absences were consistent with space groups *Pn* and *P2/n*. The |*E*| distribution statistics were indicative of a non-centrosymmetric space group: the structure was initially refined in *Pn*. Molecular symmetry and coordinate equivalence[6,7] within their e.s.d.'s suggested a centrosymmetric space group.[8,9] The number of molecules in the unit cell required twofold axis symmetry be present in the molecule for space group. *P2/n*. The reported final structure was successfully refined in the space group *P2/n*.

The intensities of three standard reflections, monitored every three hours of X-ray exposure time, showed no greater fluctuations during data collection than those expected from Poisson statistics. Intensity data were corrected for Lorentz and polarization effects, scale variation, but not for absorption and reduced to F_o^2.[10]

The structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program *DIRDIF*.[11] The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined. A subsequent difference synthesis resulted in the location of all the hydrogen atoms, which coordinates and isotropic thermal displacement parameters were refined.

Final refinement on F^2 carried out by full-matrix least-squares techniques converged at $wR(F^2)$ = 0.0667 for 3375 reflections with $F_o^2 \geq 0$ and $R(F)$ = 0.0243 for 3204 reflections with $F_o \geq 4.0$ $\sigma(F_o)$ and 2448 parameters. The final difference Fourier map did not show any significant residual features.

The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms and isotropic thermal displacement parameters for hydrogen atoms were refined on F^2 with full-matrix least-squares procedures minimizing the function $Q = \Sigma_h [w(|F_o^2 - kF_c^2|)^2]$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2,0) + 2F_c^2] / 3$, F_0 and F_c are the observed and calculated structure factor amplitudes, respectively; *a* and *b* were refined. Reflections were stated observed if satisfying $F^2 > 0$ criterion of observability.

Crystal data and numerical details on data collection and refinement are given in Table 1. Final fractional atomic coordinates equivalent displacement parameters for the non-hydrogen atoms are given in Table 2. Molecular geometry data are collected in Table 3. Tables of hydrogen atom positions, thermal displacement parameters, comprehensive distances and angles and tables of (F_o), (F_c) and $\sigma(F_o)$ are given as supplementary material[*1] for this paper. Neutral atom scattering factors and anomalous dispersion corrections were taken from

---

[1]Supplementary Material Available: Tables of crystal data, anisotropic thermal displacement parameters, atomic coordinates, bond lengths, bond angles, and torsion angles (as a *CIF*[16] file) and an *ORTEP*[17] plot; a listing of observed and calculated structure factors (also as a *CIF* file).

International Tables of Crystallography.[12] All calculations performed on the HP9000/735 computer at the University of Groningen with the program packages *SHELXL*[13] (least-square refinements), *PLATON*[14] (calculation of geometric data and the *ORTEP* illustrations) and a locally modified version of the program *PLUTO*[15] (preparation of illustrations).

Results and discussion.

The identification of the atoms and the configuration are shown in the *PLUTO* drawing of Fig. 1. Each asymmetric unit contains one half formula unit molecule with the Zr position at a twofold axis: the molecules have a crystallographic imposed twofold axis.

The monoclinic unit cell contains two discrete units of the title compound separated by normal van der Waals distances[18]

No missed symmetry (*MISSYM*) or solvent-accessible voids were detected by procedures implemented in *PLATON.*[19,20]

References.

1. Bolhuis, F. van (1971). J. Appl. Cryst. **4**, 263-264.
2. Enraf-Nonius *CAD4-UNIX* Version 5.1, Utrecht modified version October 1994. Enraf-Nonius Delft, Scientific Instruments Division, Delft, The Netherlands.
3. Duisenberg, A. J. M. (1992). J. Appl. Cryst. **25**, 92-96.
4. Boer, J. L. de & Duisenberg, A. J. M. (1984). Acta. Cryst. A**40**, C410.
5. Spek, A.L. (1988). J. Appl. Cryst. **21**, 578-579.
6. Le Page, Y. (1987). J. Appl. Cryst. **20**, 264-269.
7. Le Page, Y. (1988). J. Appl. Cryst. **21**, 983-984.
8. Marsch, R.E. & Herbstein, F.H. (1988). Acta Cryst. B**44**, 77-88.
9. Snow, M.R. & Tiekink, E.R.T. (1988). Acta Cryst. B**44**, 676-677.
10. Spek, A.L. (1993). *HELENA. Program for Reduction of CAD4 Data.* Utrecht Univ. The Netherlands.
11. Beurskens, P.T., Beurskens, G., Bosman, W.P., Gelder, R. de, García-Granda, S., Gould, R.O., Israël, R. & Smits, J.M.M., (1997). The *DIRDIF*-97 program system, Crystallography Laboratory, University of Nijmegen, The Netherlands.
12. *International Tables for Crystallography* (1992). Vol. C. Edited by A.J.C. Wilson, Kluwer Academic Publishers, Dordrecht. The Netherlands.
13. Sheldrick, G.M. (1997). *SHELX-97. Program for the Solution and Refinement of Crystal Structures.* Univ. of Göttingen, Germany.

14. Spek, A.L. (1996). *PLATON. Program for the Automated Analysis of Molecular Geometry.* Version of October 1996. Univ. of Utrecht, The Netherlands.

15. Meetsma, A. (1996*). PLUTO. Program for the Display and Analysis of Crystal and Molecular Structures.* Version of October 1996. Univ. of Groningen, The Netherlands.

16. Hall, S.R, Allen, F.H. & Brown, I.D. (1991). Acta Cryst. A**47**, 655-685.

17. Johnson, C.K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

18. Bondi, A. (1964). J. Phys. Chem. **68**, 441-451.

19. Spek, A.L. (1990). Acta Cryst. A**46**, C-34.

20. Spek, A.L. (1994). Am. Crystallogr. Assoc. Abstr. **22**, 66.

21. *International Tables for Crystallography* (1983). Vol. A. Space-group symmetry, edited by T. Hahn. Dordrecht: Reidel. (Present distributor Kluwer Academic Publishers, Dordrecht).

22. Fisher, R.X. & Tillmanns, E. (1988). Acta Cryst. C**44**, 775-776.

Legends to the Figures.

Fig. 1. *PLUTO* drawing of the molecule illustrating the puckering and the adopted numbering scheme.

Fig. 2. Perspective *ORTEP*[17] drawing of the title compound with the atom labeling scheme. All atoms are represented by their thermal displacement vibrational ellipsoids drawn to encompass 50% of the electron density. H-atoms have been omitted to improve clarity.

Table 1.

a. Crystal data and details of the structure determination.

Moiety_ Formula	$(C_{17}H_{19}N)_2Zr$
Formula_Weight, g.mol^{-1}	565.92
Crystal system	monoclinic
Space group, no.[21]	*P*2/*n*, 13
a, Å	8.718(1)
b, Å	9.278(1)
c, Å	17.567(3)
β, deg	100.12(2)
V, Å^3	1398.8(3)
Formula_*Z*	2
SpaceGroup_*Z*	4
Z' (= Formula_Z / SpaceGroup-*Z*)	0.5
ρ_{calc}, g.cm^{-3}	1.344
F(000), electrons	592
μ(Mo K$\overline{\alpha}$), cm^{-1}	4.2
color, habit	colorless,prism
Approx. crystal dimension, mm	0.45 x 0.50 x 0.52

b. Data collection.

Radiation	Mo K$\bar{\alpha}$
Wavelength, Å	0.71073
Monochromator	Graphite
Temperature, K	130
θ range; min. max., deg	1.18, 28.0
ω/2θ scan, deg	$\Delta\omega = 0.95 + 0.34$ tg θ
Index ranges	h: -11→11; k: 0→12; l: -23→23
Crystal-to-receiving-aperturedistance, mm	173
Horizontal-, vertical-aperture, mm	3.2 + tg θ; 4.0
Reference reflections,	21-1, 1.1
r.m.s. dev. in %	-1-14, 1.8
	153, 2.0
Drift correction	1.000 - 1.100
X-ray exposure time, h	107.1
Total data	7022
Unique data	3375
Data with criterion: ($F_o \geq 4.0\ \sigma\ (F_o)$)	3204
$R_{int} = \Sigma\ [\lvert F_o^2 - F_o^2\ (\text{mean})\rvert] / \Sigma\ [F_o^2]$	0.020
$R_{sig} = \Sigma\ \sigma(F_o^2) / \Sigma\ [F_o^2]$	0.008

c. Refinement.

Number of reflections ($F_o^2 \geq 0$)	3375
Number of refined parameters	244
Final agreement factors:	
$wR(F^2) = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$	0.0667
for $F_o^2 > 0$	
Weighting scheme: *a, b*	0.0389, 0.6141
$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$	
and $P = [\max(F_o^2,0) + 2F_c^2] / 3$	
$R(F) = \Sigma(\|\|F_o\| - \|F_c\|\|) / \Sigma\|F_o\|$	0.0243
for $F_o > 4.0\ \sigma(F_o)$	
GooF = S = $[\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$	1.088
n = number of reflections	
p = number of parameters refined	
Residual electron density in final	
difference Fourier map, e/Å^3	-0.64, 0.65(6)
Max. (shift/σ) final cycle	< 0.001

Table 2. Final fractional atomic coordinates and equivalent isotropic thermal displacement parameters for non-H atoms with e.s.d.'s in parentheses. Atoms of the Asymmetric Unit.

Atom	*x*	*y*	*z*	U_{eq} (Å^2)*
Zr	0.25(-)	0.06226(2)	0.25(-)	0.0185(1)
N(1)	0.01522(13)	0.15987(15)	0.17590(7)	0.0272(3)
C(1)	-0.10201(18)	0.0506(2)	0.18952(10)	0.0366(5)
C(2)	-0.0456(2)	-0.0962(2)	0.17063(9)	0.0362(5)
C(3)	0.11599(19)	-0.12014(17)	0.17870(8)	0.0297(4)
C(4)	0.1647(3)	-0.25244(18)	0.15107(9)	0.0404(5)
C(5)	0.0538(4)	-0.3548(2)	0.11968(12)	0.0609(8)
C(6)	-0.1023(4)	-0.3326(3)	0.11798(14)	0.0722(9)
C(7)	-0.1532(3)	-0.2040(3)	0.14311(12)	0.0575(7)
C(8)	0.3342(3)	-0.2857(2)	0.15362(12)	0.0508(7)
C(9)	-0.00190(19)	0.1831(2)	0.09118(9)	0.0343(5)
C(10)	-0.0061(2)	0.3015(2)	0.21167(9)	0.0353(5)
C(11)	0.01635(16)	0.28978(16)	0.29825(9)	0.0277(4)
C(12)	0.11279(15)	0.17844(16)	0.33452(8)	0.0241(4)
C(13)	0.11588(16)	0.16207(16)	0.41496(8)	0.0252(4)
C(14)	0.03666(17)	0.25919(17)	0.45521(9)	0.0291(4)
C(15)	-0.04955(18)	0.37119(18)	0.41793(10)	0.0322(4)
C(16)	-0.06249(17)	0.38539(17)	0.33858(10)	0.0308(4)
C(17)	0.1973(2)	0.03851(19)	0.46094(9)	0.0328(5)

*$U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ [22]

Table 3. Selected data on the geometry.

Standard deviations in the last decimal place are given in parentheses.

Interatomic Distances (Å)

Zr	-N(1)	2.4016(13)	C(4)	-C(8)	1.503(4)
Zr	-C(3)	2.2986(16)	C(5)	-C(6)	1.372(5)
Zr	-C(12)	2.3284(14)	C(6)	-C(7)	1.373(4)
N(1)	-C(1)	1.488(2)	C(10)	-C(11)	1.503(2)
N(1)	-C(9)	1.485(2)	C(11)	-C(12)	1.411(2)
N(1)	-C(10)	1.482(2)	C(11)	-C(16)	1.390(2)
C(1)	-C(2)	1.505(3)	C(12)	-C(13)	1.417(2)
C(2)	-C(3)	1.408(2)	C(13)	-C(14)	1.400(2)
C(2)	-C(7)	1.398(3)	C(13)	-C(17)	1.506(2)
C(3)	-C(4)	1.412(2)	C(14)	-C(15)	1.379(2)
C(4)	-C(5)	1.398(3)	C(15)	-C(16)	1.385(2)

Bond angles (deg.)

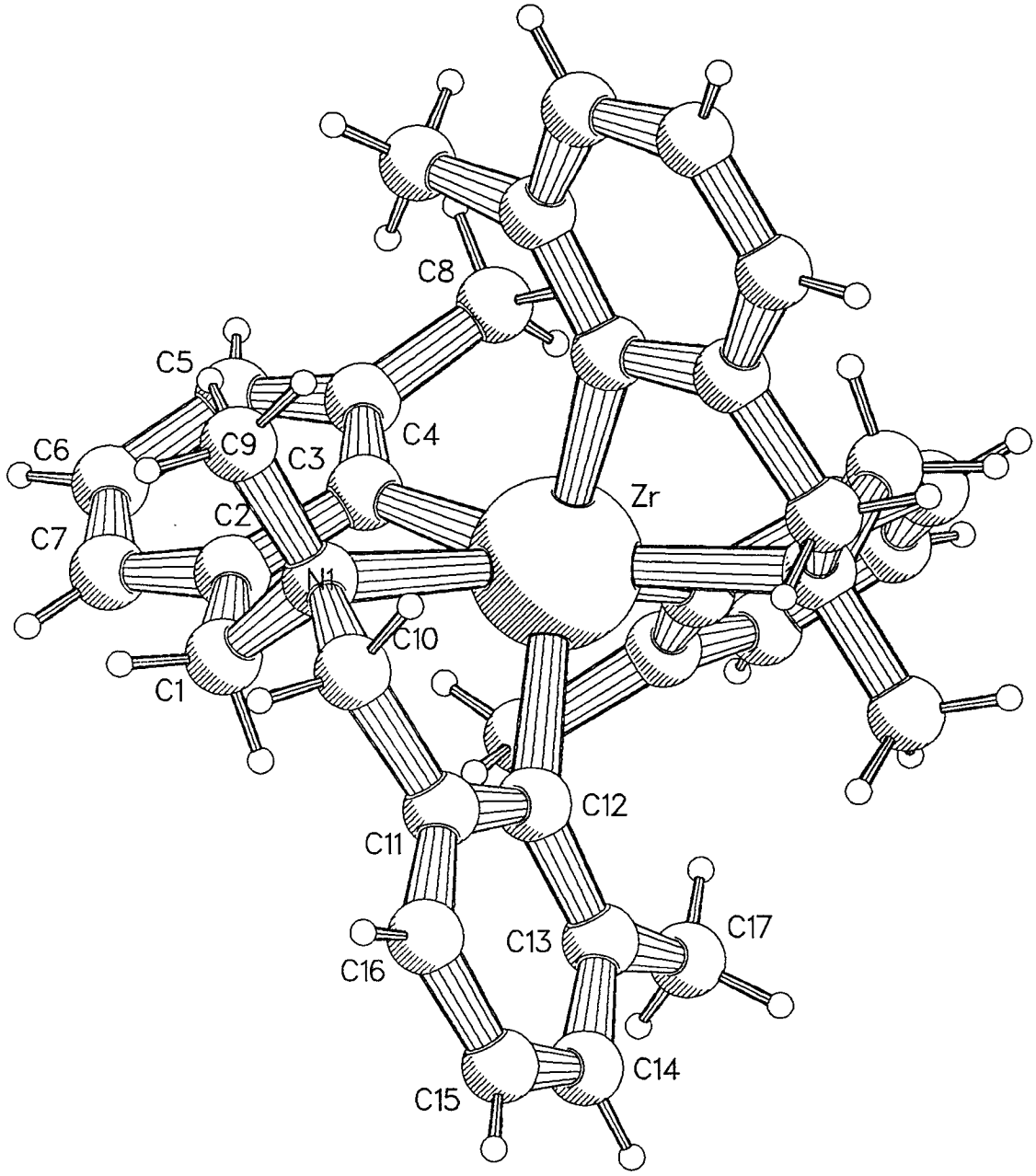
N(1)	-Zr	-C(3)	71.28(6)	C(3)	-C(2)	-C(7)	121.36(18)
N(1)	-Zr	-C(12)	71.74(5)	Zr	-C(3)	-C(2)	110.02(11)
N(1)	-Zr	-N(1)a	135.69(5)	Zr	-C(3)	-C(4)	132.25(14)
N(1)	-Zr	-C(3)a	151.18(6)	C(2)	-C(3)	-C(4)	117.27(17)
N(1)	-Zr	-C(12)a	87.95(5)	C(3)	-C(4)	-C(5)	119.8(2)
C(3)	-Zr	-C(12)	114.80(6)	C(3)	-C(4)	-C(8)	121.45(18)
C(3)	-Zr	-N(1)a	151.18(6)	C(5)	-C(4)	-C(8)	118.73(19)
C(3)	-Zr	-C(3)a	85.18(6)	C(4)	-C(5)	-C(6)	121.4(2)
C(3)	-Zr	-C(12)a	105.20(5)	C(5)	-C(6)	-C(7)	119.9(3)
C(12)	-Zr	-N(1)a	87.95(5)	C(2)	-C(7)	-C(6)	119.9(2)
C(12)	-Zr	-C(3)a	105.20(5)	N(1)	-C(10)	-C(11)	111.17(14)
C(12)	-Zr	-C(12)a	124.85(5)	C(10)	-C(11)	-C(12)	118.11(14)
N(1)a	-Zr	-C(3)a	71.28(5)	C(10)	-C(11)	-C(16)	118.78(14)
N(1)a	-Zr	-C(12)a	71.74(5)	C(12)	-C(11)	-C(16)	123.07(14)
C(3)a	-Zr	-C(12)a	114.80(6)	Zr	-C(12)	-C(11)	112.52(10)
Zr	-N(1)	-C(1)	101.53(9)	Zr	-C(12)	-C(13)	131.65(10)
Zr	-N(1)	-C(9)	121.59(9)	C(11)	-C(12)	-C(13)	115.73(13)
Zr	-N(1)	-C(10)	105.24(9)	C(12)	-C(13)	-C(14)	120.67(14)
C(1)	-N(1)	-C(9)	108.00(12)	C(12)	-C(13)	-C(17)	122.75(13)
C(1)	-N(1)	-C(10)	113.26(12)	C(14)	-C(13)	-C(17)	116.54(13)
C(9)	-N(1)	-C(10)	107.35(13)	C(13)	-C(14)	-C(15)	121.42(15)
N(1)	-C(1)	-C(2)	108.71(13)	C(14)	-C(15)	-C(16)	119.41(15)
C(1)	-C(2)	-C(3)	118.71(15)	C(11)	-C(16)	-C(15)	119.48(15)
C(1)	-C(2)	-C(7)	119.89(18)				

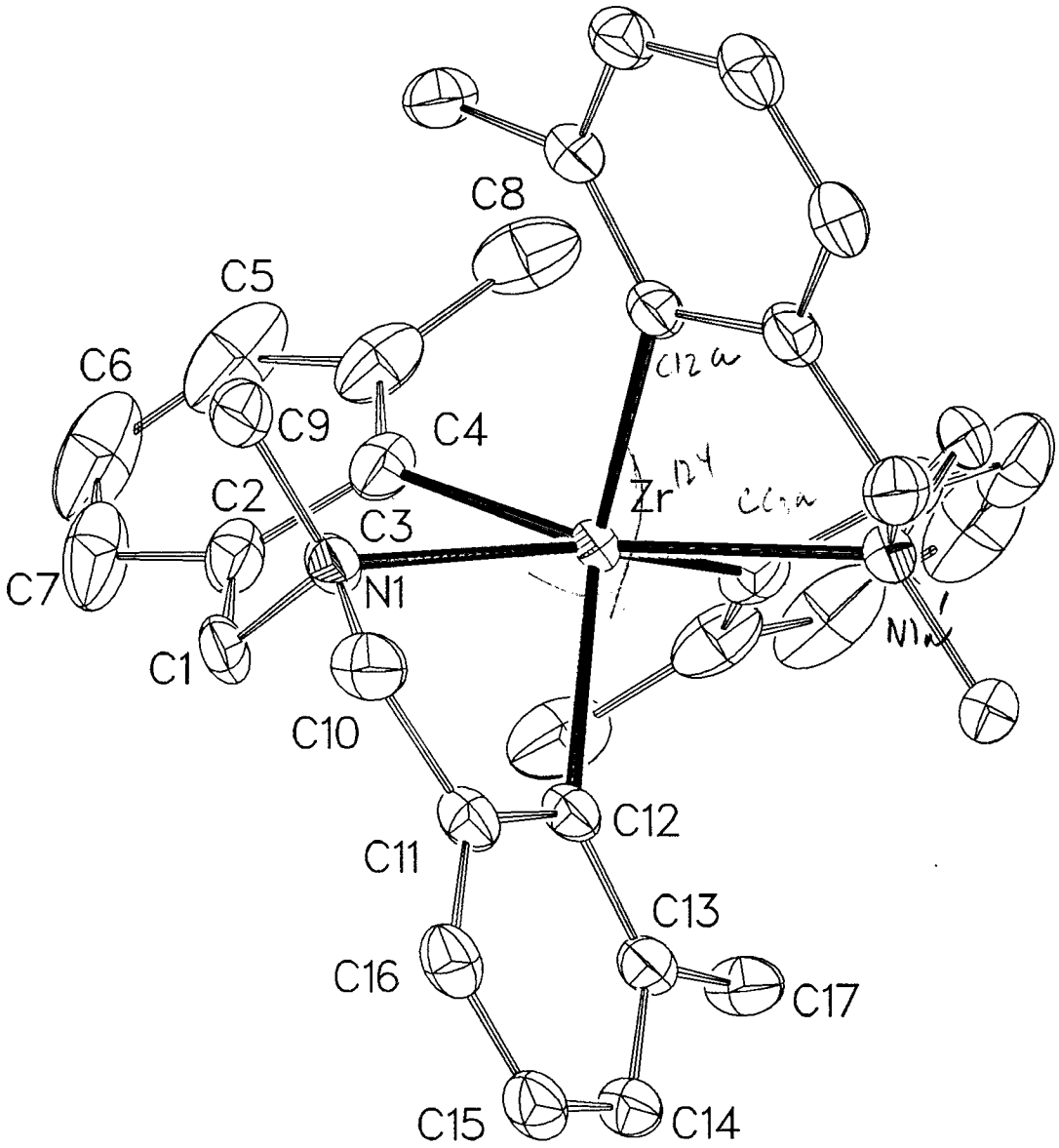
Torsion angles (deg.)

C(3)	-Zr	-N(1)	-C(1)	45.77(10)
C(3)	-Zr	-N(1)	-C(9)	-73.95(12)
C(3)	-Zr	-N(1)	-C(10)	164.02(10)
C(12)	-Zr	-N(1)	-C(1)	-79.55(10)
C(12)	-Zr	-N(1)	-C(9)	160.73(13)
C(12)	-Zr	-N(1)	-C(10)	38.70(9)
N(1)a	-Zr	-N(1)	-C(1)	-146.47(9)
N(1)a	-Zr	-N(1)	-C(9)	93.81(13)
N(1)a	-Zr	-N(1)	-C(10)	-28.22(12)
C(3)a	-Zr	-N(1)	-C(1)	8.91(15)
C(3)a	-Zr	-N(1)	-C(9)	-110.81(14)
C(3)a	-Zr	-N(1)	-C(10)	127.16(12)
C(12)a	-Zr	-N(1)	-C(1)	152.58(10)
C(12)a	-Zr	-N(1)	-C(9)	32.86(12)
C(12)a	-Zr	-N(1)	-C(10)	-89.17(10)
N(1)	-Zr	-C(3)	-C(2)	-33.01(10)
N(1)	-Zr	-C(3)	-C(4)	155.17(16)
C(12)	-Zr	-C(3)	-C(2)	25.59(12)
C(12)	-Zr	-C(3)	-C(4)	-146.23(14)
N(1)a	-Zr	-C(3)	-C(2)	164.89(10)
N(1)a	-Zr	-C(3)	-C(4)	-6.9(2)
C(3)a	-Zr	-C(3)	-C(2)	130.12(11)
C(3)a	-Zr	-C(3)	-C(4)	-41.70(15)
C(12)a	-Zr	-C(3)	-C(2)	-115.47(11)
C(12)a	-Zr	-C(3)	-C(4)	72.71(15)
N(1)	-Zr	-C(12)	-C(11)	-26.64(10)
N(1)	-Zr	-C(12)	-C(13)	157.22(15)
C(3)	-Zr	-C(12)	-C(11)	-84.99(11)
C(3)	-Zr	-C(12)	-C(13)	98.87(14)
N(1)a	-Zr	-C(12)	-C(11)	113.34(11)
N(1)a	-Zr	-C(12)	-C(13)	-62.79(14)
C(3)a	-Zr	-C(12)	-C(11)	-176.69(10)
C(3)a	-Zr	-C(12)	-C(13)	7.18(15)
C(12)a	-Zr	-C(12)	-C(11)	47.36(12)
C(12)a	-Zr	-C(12)	-C(13)	-128.78(13)
Zr	-N(1)	-C(1)	-C(2)	-52.39(13)
C(9)	-N(1)	-C(1)	-C(2)	76.55(16)
C(10)	-N(1)	-C(1)	-C(2)	-164.71(13)
Zr	-N(1)	-C(10)	-C(11)	-46.63(14)
C(1)	-N(1)	-C(10)	-C(11)	63.40(17)
C(9)	-N(1)	-C(10)	-C(11)	-177.48(13)
N(1)	-C(1)	-C(2)	-C(3)	28.0(2)
N(1)	-C(1)	-C(2)	-C(7)	-149.80(16)
C(1)	-C(2)	-C(3)	-Zr	14.86(17)
C(1)	-C(2)	-C(3)	-C(4)	-171.94(14)
C(7)	-C(2)	-C(3)	-Zr	-167.36(14)
C(7)	-C(2)	-C(3)	-C(4)	5.8(2)
C(1)	-C(2)	-C(7)	-C(6)	172.94(19)
C(3)	-C(2)	-C(7)	-C(6)	-4.8(3)
Zr	-C(3)	-C(4)	-C(5)	169.31(13)
Zr	-C(3)	-C(4)	-C(8)	-11.5(2)

C(2)	-C(3)	-C(4)	-C(5)	-2.0(2)
C(2)	-C(3)	-C(4)	-C(8)	177.17(15)
C(3)	-C(4)	-C(5)	-C(6)	-2.9(3)
C(8)	-C(4)	-C(5)	-C(6)	177.91(19)
C(4)	-C(5)	-C(6)	-C(7)	4.0(3)
C(5)	-C(6)	-C(7)	-C(2)	-0.2(3)
N(1)	-C(10)	-C(11)	-C(12)	26.39(19)
N(1)	-C(10)	-C(11)	-C(16)	-151.45(14)
C(10)	-C(11)	-C(12)	-Zr	10.10(17)
C(10)	-C(11)	-C(12)	-C(13)	-173.10(14)
C(16)	-C(11)	-C(12)	-Zr	-172.15(12)
C(16)	-C(11)	-C(12)	-C(13)	4.6(2)
C(10)	-C(11)	-C(16)	-C(15)	176.60(15)
C(12)	-C(11)	-C(16)	-C(15)	-1.1(2)
Zr	-C(12)	-C(13)	-C(14)	171.24(11)
Zr	-C(12)	-C(13)	-C(17)	-11.3(2)
C(11)	-C(12)	-C(13)	-C(14)	-4.8(2)
C(11)	-C(12)	-C(13)	-C(17)	172.71(14)
C(12)	-C(13)	-C(14)	-C(15)	1.6(2)
C(17)	-C(13)	-C(14)	-C(15)	-176.07(15)
C(13)	-C(14)	-C(15)	-C(16)	2.2(2)
C(14)	-C(15)	-C(16)	-C(11)	-2.4(2)

The sign of the torsion angle is positive if when looking from atom-2 to atom-3 a clockwise motion of atom-1 would superimpose it on atom-4.


C8
C5
C6
C9
C4
C3
C7
C2
Zr
N1
C10
C1
C12
C11
C13
C17
C16
C14
C15


C8
C5
C6
C9
C4
C2
C3
C7
N1
C1
C10
C12a
Zr1
C12
C11
C13
C16
C17
C15
C14

Supporting Material to:

"Highly Electron-Deficient Neutral and Cationic Zirconium Complexes with bis(σ-aryl)-amine Dianionic Tridentate Ligands "

by M. Bouwkamp, D. van Leusen, A. Meetsma, and B. Hessen

Part III: Structure of {[(C$_9$H$_6$)CH$_2$]$_2$NMe]Zr(CH$_2$Ph)$_2$ (3).

Abstract. "IUPAC-name", $C_{37}H_{33}NZr$, M = 582.90, monoclinic, $P2_1/c$, a = 16.587(3), b = 11.016(1), c = 15.870(3) Å,β = 105.96(3)°, V = 2788.0(9) Å^3 Z = 4, D_x = 1.389 g cm^{-3}, λ(MoKα) = 0.71073 Å, μ = 4.2 cm^{-1}, F(000) = 1208, T = 130 K, $wR(F^2)$ = 0.1910 for 5565 reflections with $F_o^2 \geq 0$ and 484 parameters and $R(F)$ = 0.0717 for 3615 reflections obeying $F_o \geq 4.0\ \sigma(F_o)$ criterion of observability.

The asymmetric unit consists one molecule of the title compound.

Experimental

X-ray diffraction: Crystal and Molecular Structure.

Suitable yellowish colored block-shaped crystals were obtained by recrystallisation from ....

The crystal, a parallelepiped of approximate size 0.15 x 0.25 x 0.30 mm., used for characterization and data collection was mounted on top of a glass fiber by using inert-atmosphere handling techniques and was transferred into the cold nitrogen cold stream of the low temperature unit[1] mounted on an Enraf-Nonius *CAD-4F*^{2} diffractometer, interfaced to a *INDY* (*Silcon Graphics*) *UNIX* computer (Mo tube, 50 kV, 40 mA, monochromated Mo-Kα radiation, $\Delta\omega = 1.10 + 0.34\ \mathrm{tg}\ \theta$).

Reflections profiles showed large mosaicity; this mosaicity did not allow to use a narrower scan angle.The scattering power of the studied crystals was weak.

The unit cell was identified as monoclinic; reduced cell calculations did not indicate any higher metric lattice symmetry.[5] The space group $P2_1/c$ was derived from the systematic extinctions. Examination of the final atomic coordinates of the structure did not yield extra metric symmetry elements.[6,7]

Intensity data were corrected for Lorentz and polarization effects, scale variation, but not for absorption and reduced to F_o^2.[8]

The structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program *DIRDIF*.[9] The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined. A subsequent difference Fourier synthesis resulted in the location of all the hydrogen atoms, which coordinates and isotropic thermal displacement parameters were refined.

Final refinement on F^2 carried out by full-matrix least-squares techniques converged at $wR(F^2)$ = 0.1910 for 5465 reflections with $F_o^2 \geq 0$ and $R(F)$ = 0.0717 for 3615 reflections with $F_o \geq 4.0$ $\sigma(F_o)$ and 484 parameters.

The final difference Fourier map was essentially featureless with a few peaks of max. 1.73(14) e/Å^3.within 1.0 Å from Zr, but were neglected/rejected, being artefacts. No other significant peaks having chemical meaning above the general background were observed in the final difference Fourier syntheses.

The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms and isotropic thermal displacement parameters for hydrogen atoms were refined on F^2 with full-matrix least-squares procedures minimizing the function $Q = \Sigma_h [w(|F_o^2 - kF_c^2|)^2]$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2,0) + 2F_c^2] / 3$, F_o and F_c are the observed and calculated structure factor amplitudes, respectively; a and b were refined. Reflections were stated observed if satisfying $F^2 > 0$ criterion of observability.

Crystal data and numerical details on data collection and refinement are given in Table 1. Final fractional atomic coordinates equivalent displacement parameters for the non-hydrogen atoms are given in Table 2. Molecular geometry data are collected in Table 3. Tables of hydrogen atom positions, thermal displacement parameters, comprehensive distances and angles and tables of (F_o), (F_c) and $\sigma(F_o)$ are given as supplementary material[*1] for this paper. Neutral atom scattering factors and anomalous dispersion corrections were taken from *International Tables of Crystallography*.[10] All calculations performed on the HP9000/735 computer at the University of Groningen with the program packages *SHELXL*[11] (least-square refinements), *PLATON*[12] (calculation of geometric data and the *ORTEP* illustrations) and a locally modified version of the program *PLUTO*[13] (preparation of illustrations).

[*1]Supplementary Material Available: Tables of crystal data, anisotropic thermal displacement parameters, atomic coordinates, bond lengths, bond angles, and torsion angles (as a *CIF*[14] file) and an *ORTEP*[15] plot; a listing of observed and calculated structure factors (also as a *CIF* file).

Results and discussion.

The identification of the atoms and the configuration are shown in the *PLUTO* drawing of Fig. 1.; Each asymmetric unit contains one formula unit molecule with no atom setting at special position. The monoclinic unit cell contains four discrete units of the title compound separated by normal van der Waals distances[16].

No missed symmetry (*MISSYM*) or solvent-accessible voids were detected by procedures implemented in *PLATON.*[17,18]

References.

1. Bolhuis, F. van (1971). J. Appl. Cryst. **4**, 263-264.
2. Enraf-Nonius *CAD4-UNIX* Version 5.1, Utrecht modified version October 1994. Enraf-Nonius Delft, Scientific Instruments Division, Delft, The Netherlands.
3. Duisenberg, A. J. M. (1992). J. Appl. Cryst. **25**, 92-96.
4. Boer, J. L. de & Duisenberg, A. J. M. (1984). Acta. Cryst. A**40**, C410.
5. Spek, A.L. (1988). J. Appl. Cryst. **21**, 578-579.
6. Le Page, Y. (1987). J. Appl. Cryst. **20**, 264-269.
7. Le Page, Y. (1988). J. Appl. Cryst. **21**, 983-984.
8. Spek, A.L. (1993). *HELENA. Program for Reduction of CAD4 Data.* Utrecht Univ. The Netherlands.
9. Beurskens, P.T., Beurskens, G., Bosman, W.P., Gelder, R. de, García-Granda, S., Gould, R.O., Israël, R. & Smits, J.M.M., (1997). The *DIRDIF*-97 program system, Crystallography Laboratory, University of Nijmegen, The Netherlands.
10. *International Tables for Crystallography* (1992). Vol. C. Edited by A.J.C. Wilson, Kluwer Academic Publishers, Dordrecht. The Netherlands.
11. Sheldrick, G.M. (1997). *SHELX-97. Program for the Solution and Refinement of Crystal Structures.* Univ. of Göttingen, Germany.
12. Spek, A.L. (1996). *PLATON. Program for the Automated Analysis of Molecular Geometry.* Version of October 1996. Univ. of Utrecht, The Netherlands.
13. Meetsma, A. (1996*). PLUTO. Program for the Display and Analysis of Crystal and Molecular Structures.* Version of October 1996. Univ. of Groningen, The Netherlands.
14. Hall, S.R, Allen, F.H. & Brown, I.D. (1991). Acta Cryst. A**47**, 655-685.
15. Johnson, C.K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
16. Bondi, A. (1964). J. Phys. Chem. **68**, 441-451.

17. Spek, A.L. (1990). Acta Cryst. A**46**, C-34.

18. Spek, A.L. (1994). Am. Crystallogr. Assoc. Abstr. **22**, 66.

19. *International Tables for Crystallography* (1983). Vol. A. Space-group symmetry, edited by T. Hahn. Dordrecht: Reidel. (Present distributor Kluwer Academic Publishers, Dordrecht).

20. Fisher, R.X. & Tillmanns, E. (1988). Acta Cryst. C**44**, 775-776.

Legends to the Figures.

Fig. 1. *PLUTO* drawing of the molecule illustrating the puckering and the adopted numbering scheme.

Fig. 2. Perspective *ORTEP*[14] drawing of the title compound with the atom labeling scheme. All atoms are represented by their thermal displacement vibrational ellipsoids drawn to encompass 50% of the electron density. Hydrogen atoms are drawn as spheres of arbitrary radius.

Table 1.

a. Crystal data and details of the structure determination.

Moiety_ Formula	$C_{37}H_{33}NZr$
Formula_Weight, g.mol^{-1}	582.90
Crystal system	monoclinic
Space group, no.[19]	$P2_1/c$, 14
a, Å	16.587(3)
b, Å	11.016(1)
c, Å	15.870(2)
β, deg	105.96(3)
V, Å^3	2788.0(9)
Formula_*Z*	4
SpaceGroup_*Z*	4
Z' (= Formula_Z / SpaceGroup-*Z*)	1
ρ_{calc}, g.cm^{-3}	1.389
F(000), electrons	1208
μ(Mo K$\bar{\alpha}$), cm^{-1}	4.2
color, habit	yellow, rectangle
Approx. crystal dimension, mm	0.15 x 0.25 x 0.30

b. Data collection.

Radiation	Mo K$\bar{\alpha}$
Wavelength, Å	0.71073
Monochromator	Graphite
Temperature, K	130
θ range; min. max., deg	1.28, 26.0
ω/2θ scan, deg	$\Delta\omega = 1.10 + 0.34 \text{ tg } \theta$
Index ranges	h: -20→19; k: 0→13; l: 0→19
Crystal-to-receiving-aperturedistance, mm	173
Horizontal-, vertical-aperture, mm	3.2 + tg θ; 4.0
Reference reflections,	-204, 2.5
r.m.s. dev. in %	222, 1.3
	-2-2-2,1.5
Drift correction	1.000 - 1.010
X-ray exposure time, h	102.7
Total data	5989
Unique data	5466
Data with criterion: ($F_o \geq 4.0\ \sigma\ (F_o)$)	3615
$R_{int} = \Sigma\ [\lvert F_o^2 - F_o^2\ (\text{mean})\rvert] / \Sigma\ [F_o^2]$	0.067
$R_{sig} = \Sigma\ \sigma(F_o^2) / \Sigma\ [F_o^2]$	0.073

c. Refinement.

Number of reflections ($F_o^2 \geq 0$)	5465
Number of refined parameters	484
Final agreement factors:	
$wR(F^2) = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$	0.1910
for $F_o^2 > 0$	
Weighting scheme: *a, b*	0.1268, 0
$w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$	
and $P = [\max(F_o^2,0) + 2F_c^2] / 3$	
$R(F) = \Sigma(\|\|F_o\| - \|F_c\|\|) / \Sigma\|F_o\|$	0.0717
for $F_o > 4.0\ \sigma(F_o)$	
GooF = S = $[\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$	0.980
n = number of reflections	
p = number of parameters refined	
Residual electron density in final	
difference Fourier map, e/Å^3	-2.17, 1.73(14)
Max. (shift/σ) final cycle	< 0.001

Table 2. Final fractional atomic coordinates and equivalent isotropic thermal displacement parameters for non-H atoms with e.s.d.'s in parentheses. Atoms of the Asymmetric Unit.

Atom	*x*	*y*	*z*	U_{eq} (Å^2)*
Zr	0.23107(3)	0.17321(5)	0.07883(4)	0.0212(2)
N	0.3336(3)	0.1365(4)	0.2139(3)	0.0258(16)
C(1)	0.3798(4)	0.2484(6)	0.2520(4)	0.034(2)
C(2)	0.3260(4)	0.3575(5)	0.2308(4)	0.0298(17)
C(3)	0.3496(4)	0.4638(7)	0.2780(5)	0.041(2)
C(4)	0.3060(5)	0.5688(6)	0.2546(5)	0.041(2)
C(5)	0.2352(4)	0.5728(6)	0.1799(4)	0.0303(19)
C(6)	0.1901(4)	0.6809(6)	0.1521(5)	0.036(2)
C(7)	0.1250(4)	0.6850(6)	0.0786(5)	0.0356(19)
C(8)	0.1010(4)	0.5799(6)	0.0301(5)	0.0347(19)
C(9)	0.1432(4)	0.4730(6)	0.0558(4)	0.0316(19)
C(10)	0.2113(4)	0.4637(5)	0.1301(4)	0.0265(17)
C(11)	0.2569(4)	0.3515(5)	0.1566(4)	0.0267(17)
C(12)	0.3934(4)	0.0385(6)	0.2095(5)	0.034(2)
C(13)	0.3527(4)	-0.0538(6)	0.1436(4)	0.0308(19)
C(14)	0.3905(4)	-0.1698(6)	0.1461(5)	0.038(2)
C(15)	0.3601(4)	-0.2494(6)	0.0799(5)	0.036(2)
C(16)	0.2910(4)	-0.2203(6)	0.0081(4)	0.0287(19)
C(17)	0.2605(5)	-0.3023(6)	-0.0615(5)	0.036(2)
C(18)	0.1940(5)	-0.2744(6)	-0.1289(5)	0.036(2)
C(19)	0.1543(4)	-0.1600(6)	-0.1318(4)	0.0311(17)
C(20)	0.1831(3)	-0.0790(6)	-0.0650(4)	0.0286(17)
C(21)	0.2524(3)	-0.1057(5)	0.0078(4)	0.0246(17)
C(22)	0.2825(4)	-0.0195(5)	0.0764(4)	0.0268(17)
C(23)	0.2801(4)	0.0954(6)	0.2702(5)	0.0326(19)
C(24)	0.0926(4)	0.1412(6)	0.0602(5)	0.0317(19)
C(25)	0.0740(3)	0.1392(5)	0.1464(4)	0.0273(19)
C(26)	0.0705(4)	0.2458(6)	0.1927(4)	0.0301(19)
C(27)	0.0587(4)	0.2435(6)	0.2749(5)	0.034(2)
C(28)	0.0494(4)	0.1351(7)	0.3142(5)	0.038(2)
C(29)	0.0525(4)	0.0273(7)	0.2697(5)	0.040(2)
C(30)	0.0654(4)	0.0300(6)	0.1884(5)	0.036(2)
C(31)	0.2586(4)	0.2371(6)	-0.0429(4)	0.0303(19)
C(32)	0.3490(4)	0.2604(6)	-0.0055(4)	0.0271(17)
C(33)	0.3789(4)	0.3748(6)	0.0283(4)	0.0307(19)
C(34)	0.4630(4)	0.3938(7)	0.0690(5)	0.036(2)
C(35)	0.5197(4)	0.3006(7)	0.0756(5)	0.045(2)
C(36)	0.4922(4)	0.1878(7)	0.0447(5)	0.046(2)
C(37)	0.4082(4)	0.1693(6)	0.0038(5)	0.035(2)

*$U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ [20]

Table 3. Selected data on the geometry.

Standard deviations in the last decimal place are given in parentheses.

Interatomic Distances (Å)

Zr	-N	2.376(5)	C(14)	-C(15)	1.355(10)
Zr	-C(11)	2.296(6)	C(15)	-C(16)	1.413(10)
Zr	-C(22)	2.292(6)	C(16)	-C(17)	1.409(10)
Zr	-C(24)	2.261(7)	C(16)	-C(21)	1.415(9)
Zr	-C(31)	2.218(6)	C(17)	-C(18)	1.344(11)
N	-C(1)	1.489(8)	C(18)	-C(19)	1.417(10)
N	-C(12)	1.481(8)	C(19)	-C(20)	1.367(9)
N	-C(23)	1.492(9)	C(20)	-C(21)	1.419(8)
C(1)	-C(2)	1.479(9)	C(21)	-C(22)	1.427(8)
C(2)	-C(3)	1.387(10)	C(24)	-C(25)	1.483(10)
C(2)	-C(11)	1.401(9)	C(25)	-C(26)	1.395(9)
C(3)	-C(4)	1.361(10)	C(25)	-C(30)	1.401(9)
C(4)	-C(5)	1.422(10)	C(26)	-C(27)	1.372(10)
C(5)	-C(6)	1.411(9)	C(27)	-C(28)	1.375(10)
C(5)	-C(10)	1.433(9)	C(28)	-C(29)	1.390(11)
C(6)	-C(7)	1.355(11)	C(29)	-C(30)	1.365(11)
C(7)	-C(8)	1.387(10)	C(31)	-C(32)	1.476(10)
C(8)	-C(9)	1.373(9)	C(32)	-C(33)	1.406(9)
C(9)	-C(10)	1.394(9)	C(32)	-C(37)	1.383(10)
C(10)	-C(11)	1.450(8)	C(33)	-C(34)	1.383(10)
C(12)	-C(13)	1.482(10)	C(34)	-C(35)	1.377(10)
C(13)	-C(14)	1.419(9)	C(35)	-C(36)	1.367(11)
C(13)	-C(22)	1.398(9)	C(36)	-C(37)	1.381(10)

Bond angles (deg.)

N	-Zr	-C(11)	71.29(19)	C(12)	-C(13)	-C(14)	119.1(6)
N	-Zr	-C(22)	71.35(19)	C(12)	-C(13)	-C(22)	118.4(6)
N	-Zr	-C(24)	122.7(2)	C(14)	-C(13)	-C(22)	122.3(6)
N	-Zr	-C(31)	124.9(2)	C(13)	-C(14)	-C(15)	119.6(7)
C(11)	-Zr	-C(22)	141.8(2)	C(14)	-C(15)	-C(16)	121.7(6)
C(11)	-Zr	-C(24)	103.7(2)	C(15)	-C(16)	-C(17)	121.6(6)
C(11)	-Zr	-C(31)	98.3(2)	C(15)	-C(16)	-C(21)	118.1(6)
C(22)	-Zr	-C(24)	102.9(2)	C(17)	-C(16)	-C(21)	120.3(6)
C(22)	-Zr	-C(31)	96.5(2)	C(16)	-C(17)	-C(18)	121.1(6)
C(24)	-Zr	-C(31)	112.4(3)	C(17)	-C(18)	-C(19)	120.1(6)
Zr	-N	-C(1)	112.7(3)	C(18)	-C(19)	-C(20)	119.7(6)
Zr	-N	-C(12)	113.8(4)	C(19)	-C(20)	-C(21)	121.9(6)
Zr	-N	-C(23)	101.3(4)	C(16)	-C(21)	-C(20)	116.9(5)
C(1)	-N	-C(12)	110.2(5)	C(16)	-C(21)	-C(22)	121.9(5)
C(1)	-N	-C(23)	109.4(5)	C(20)	-C(21)	-C(22)	121.2(5)
C(12)	-N	-C(23)	108.9(5)	Zr	-C(22)	-C(13)	118.3(4)
N	-C(1)	-C(2)	111.7(5)	Zr	-C(22)	-C(21)	125.1(4)
C(1)	-C(2)	-C(3)	120.0(6)	C(13)	-C(22)	-C(21)	116.5(5)
C(1)	-C(2)	-C(11)	117.1(5)	Zr	-C(24)	-C(25)	110.1(4)
C(3)	-C(2)	-C(11)	122.5(6)	C(24)	-C(25)	-C(26)	121.5(5)
C(2)	-C(3)	-C(4)	121.4(7)	C(24)	-C(25)	-C(30)	121.7(6)
C(3)	-C(4)	-C(5)	120.6(6)	C(26)	-C(25)	-C(30)	116.6(6)
C(4)	-C(5)	-C(6)	122.2(6)	C(25)	-C(26)	-C(27)	121.5(6)
C(4)	-C(5)	-C(10)	118.3(6)	C(26)	-C(27)	-C(28)	120.7(7)
C(6)	-C(5)	-C(10)	119.5(6)	C(27)	-C(28)	-C(29)	119.1(7)
C(5)	-C(6)	-C(7)	121.7(6)	C(28)	-C(29)	-C(30)	119.9(7)
C(6)	-C(7)	-C(8)	119.3(6)	C(25)	-C(30)	-C(29)	122.1(6)
C(7)	-C(8)	-C(9)	120.4(7)	Zr	-C(31)	-C(32)	97.7(4)
C(8)	-C(9)	-C(10)	122.8(6)	C(31)	-C(32)	-C(33)	121.5(6)
C(5)	-C(10)	-C(9)	116.2(5)	C(31)	-C(32)	-C(37)	122.0(6)
C(5)	-C(10)	-C(11)	120.8(6)	C(33)	-C(32)	-C(37)	116.4(6)
C(9)	-C(10)	-C(11)	123.0(5)	C(32)	-C(33)	-C(34)	121.3(6)
Zr	-C(11)	-C(2)	118.7(4)	C(33)	-C(34)	-C(35)	120.2(7)
Zr	-C(11)	-C(10)	124.6(4)	C(34)	-C(35)	-C(36)	119.8(7)
C(2)	-C(11)	-C(10)	116.4(5)	C(35)	-C(36)	-C(37)	119.8(7)
N	-C(12)	-C(13)	110.6(6)	C(32)	-C(37)	-C(36)	122.5(6)

Torsion angles (deg.)

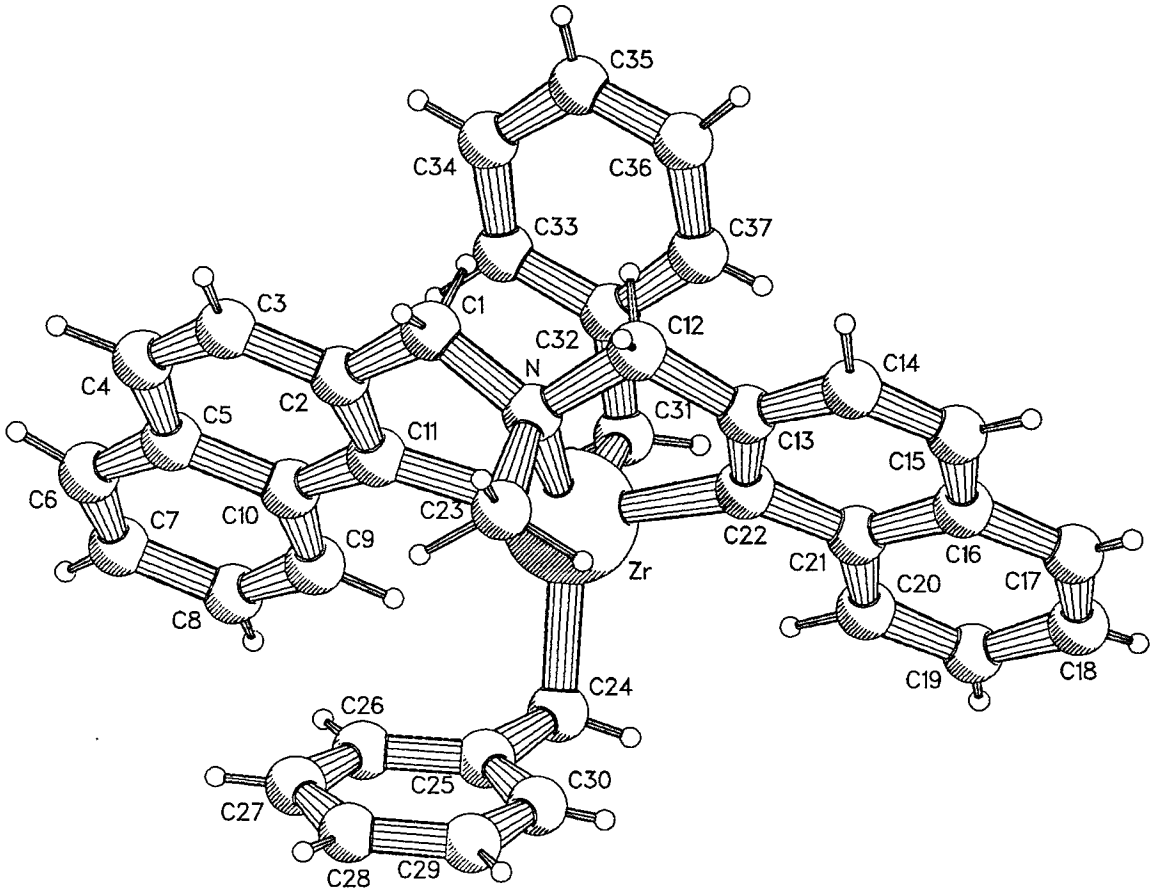
C(11)	-Zr	-N	-C(1)	-23.5(4)
C(11)	-Zr	-N	-C(12)	-150.0(4)
C(11)	-Zr	-N	-C(23)	93.4(4)
C(22)	-Zr	-N	-C(1)	148.4(4)
C(22)	-Zr	-N	-C(12)	21.9(4)
C(22)	-Zr	-N	-C(23)	-94.8(4)
C(24)	-Zr	-N	-C(1)	-118.0(4)
C(24)	-Zr	-N	-C(12)	115.5(4)
C(24)	-Zr	-N	-C(23)	-1.2(4)
C(31)	-Zr	-N	-C(1)	63.6(5)
C(31)	-Zr	-N	-C(12)	-62.9(5)
C(31)	-Zr	-N	-C(23)	-179.6(4)
N	-Zr	-C(11)	-C(2)	11.7(5)
N	-Zr	-C(11)	-C(10)	-174.4(6)
C(22)	-Zr	-C(11)	-C(2)	-0.8(7)
C(22)	-Zr	-C(11)	-C(10)	173.1(5)
C(24)	-Zr	-C(11)	-C(2)	132.0(5)
C(24)	-Zr	-C(11)	-C(10)	-54.1(6)
C(31)	-Zr	-C(11)	-C(2)	-112.4(5)
C(31)	-Zr	-C(11)	-C(10)	61.5(6)
N	-Zr	-C(22)	-C(13)	-9.7(5)
N	-Zr	-C(22)	-C(21)	175.2(6)
C(11)	-Zr	-C(22)	-C(13)	2.7(7)
C(11)	-Zr	-C(22)	-C(21)	-172.3(4)
C(24)	-Zr	-C(22)	-C(13)	-130.3(5)
C(24)	-Zr	-C(22)	-C(21)	54.7(6)
C(31)	-Zr	-C(22)	-C(13)	115.0(5)
C(31)	-Zr	-C(22)	-C(21)	-60.1(5)
N	-Zr	-C(24)	-C(25)	20.2(5)
C(11)	-Zr	-C(24)	-C(25)	-56.1(5)
C(22)	-Zr	-C(24)	-C(25)	96.2(4)
C(31)	-Zr	-C(24)	-C(25)	-161.2(4)
N	-Zr	-C(31)	-C(32)	-7.2(5)
C(11)	-Zr	-C(31)	-C(32)	65.7(4)
C(22)	-Zr	-C(31)	-C(32)	-78.9(4)
C(24)	-Zr	-C(31)	-C(32)	174.3(4)
Zr	-N	-C(1)	-C(2)	32.5(6)
C(12)	-N	-C(1)	-C(2)	160.9(5)
C(23)	-N	-C(1)	-C(2)	-79.4(6)
Zr	-N	-C(12)	-C(13)	-30.6(6)
C(1)	-N	-C(12)	-C(13)	-158.4(5)
C(23)	-N	-C(12)	-C(13)	81.5(7)
N	-C(1)	-C(2)	-C(3)	163.3(6)
N	-C(1)	-C(2)	-C(11)	-23.4(8)
C(1)	-C(2)	-C(3)	-C(4)	173.4(7)
C(11)	-C(2)	-C(3)	-C(4)	0.4(11)
C(1)	-C(2)	-C(11)	-Zr	2.2(8)
C(1)	-C(2)	-C(11)	-C(10)	-172.2(6)
C(3)	-C(2)	-C(11)	-Zr	175.4(5)
C(3)	-C(2)	-C(11)	-C(10)	1.(1)

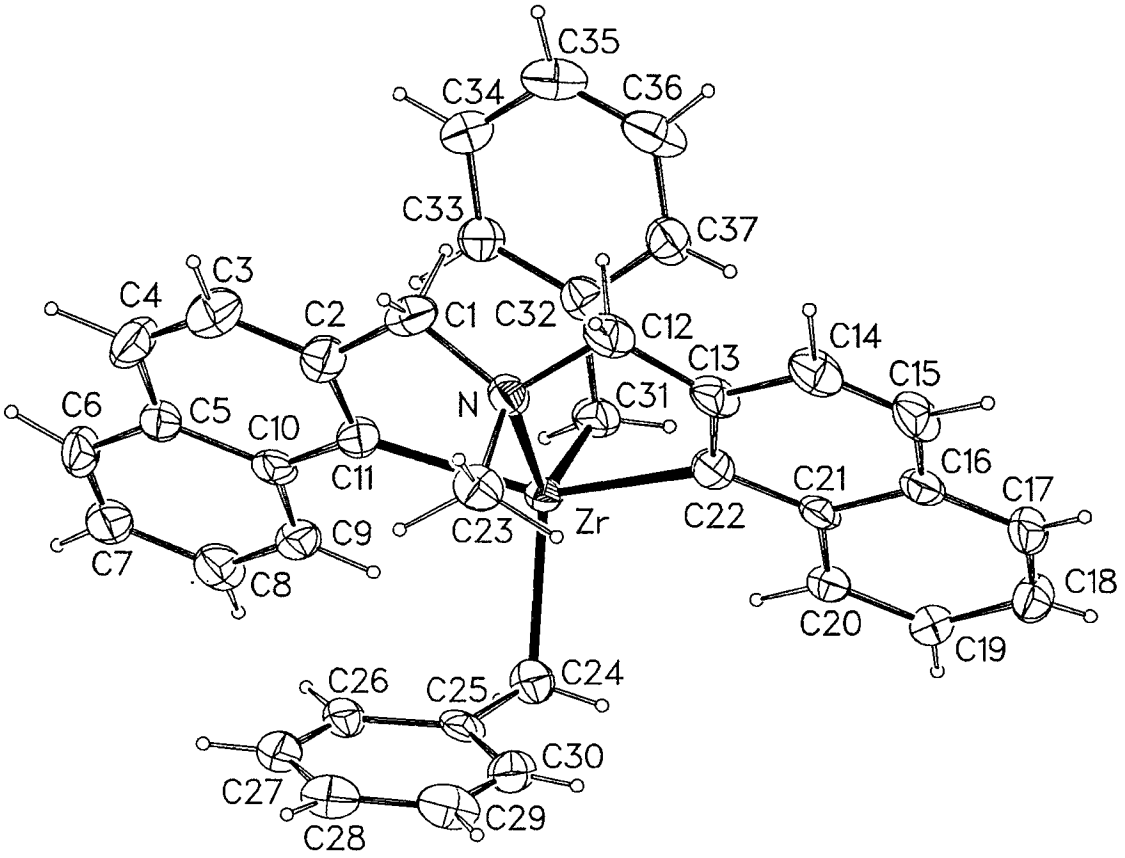
C(2)	-C(3)	-C(4)	-C(5)	-0.8(12)
C(3)	-C(4)	-C(5)	-C(6)	-178.0(7)
C(3)	-C(4)	-C(5)	-C(10)	-0.1(11)
C(4)	-C(5)	-C(6)	-C(7)	177.0(7)
C(10)	-C(5)	-C(6)	-C(7)	-0.8(10)
C(4)	-C(5)	-C(10)	-C(9)	-178.0(6)
C(4)	-C(5)	-C(10)	-C(11)	1.6(10)
C(6)	-C(5)	-C(10)	-C(9)	-0.1(9)
C(6)	-C(5)	-C(10)	-C(11)	179.5(6)
C(5)	-C(6)	-C(7)	-C(8)	1.1(11)
C(6)	-C(7)	-C(8)	-C(9)	-0.6(11)
C(7)	-C(8)	-C(9)	-C(10)	-0.3(11)
C(8)	-C(9)	-C(10)	-C(5)	0.6(10)
C(8)	-C(9)	-C(10)	-C(11)	-178.9(7)
C(5)	-C(10)	-C(11)	-Zr	-176.0(5)
C(5)	-C(10)	-C(11)	-C(2)	-2.0(9)
C(9)	-C(10)	-C(11)	-Zr	3.5(9)
C(9)	-C(10)	-C(11)	-C(2)	177.5(6)
N	-C(12)	-C(13)	-C(14)	-162.6(6)
N	-C(12)	-C(13)	-C(22)	23.1(8)
C(12)	-C(13)	-C(14)	-C(15)	-171.6(7)
C(22)	-C(13)	-C(14)	-C(15)	2.5(11)
C(12)	-C(13)	-C(22)	-Zr	-3.9(8)
C(12)	-C(13)	-C(22)	-C(21)	171.6(6)
C(14)	-C(13)	-C(22)	-Zr	-178.0(5)
C(14)	-C(13)	-C(22)	-C(21)	-2.5(10)
C(13)	-C(14)	-C(15)	-C(16)	-0.4(11)
C(14)	-C(15)	-C(16)	-C(17)	178.8(7)
C(14)	-C(15)	-C(16)	-C(21)	-1.5(10)
C(15)	-C(16)	-C(17)	-C(18)	179.1(7)
C(21)	-C(16)	-C(17)	-C(18)	-0.7(11)
C(15)	-C(16)	-C(21)	-C(20)	-179.9(6)
C(15)	-C(16)	-C(21)	-C(22)	1.4(9)
C(17)	-C(16)	-C(21)	-C(20)	-0.1(9)
C(17)	-C(16)	-C(21)	-C(22)	-178.9(6)
C(16)	-C(17)	-C(18)	-C(19)	1.3(12)
C(17)	-C(18)	-C(19)	-C(20)	-1.1(11)
C(18)	-C(19)	-C(20)	-C(21)	0.3(10)
C(19)	-C(20)	-C(21)	-C(16)	0.3(9)
C(19)	-C(20)	-C(21)	-C(22)	179.1(6)
C(16)	-C(21)	-C(22)	-Zr	175.7(5)
C(16)	-C(21)	-C(22)	-C(13)	0.6(9)
C(20)	-C(21)	-C(22)	-Zr	-3.0(8)
C(20)	-C(21)	-C(22)	-C(13)	-178.1(6)
Zr	-C(24)	-C(25)	-C(26)	76.2(6)
Zr	-C(24)	-C(25)	-C(30)	-98.9(6)
C(24)	-C(25)	-C(26)	-C(27)	-175.7(6)
C(30)	-C(25)	-C(26)	-C(27)	-0.4(9)
C(24)	-C(25)	-C(30)	-C(29)	176.6(6)
C(26)	-C(25)	-C(30)	-C(29)	1.3(10)
C(25)	-C(26)	-C(27)	-C(28)	-0.4(11)
C(26)	-C(27)	-C(28)	-C(29)	0.3(12)
C(27)	-C(28)	-C(29)	-C(30)	0.6(11)

C(28)	-C(29)	-C(30)	-C(25)	-1.4(11)
Zr	-C(31)	-C(32)	-C(33)	-91.2(6)
Zr	-C(31)	-C(32)	-C(37)	84.2(6)
C(31)	-C(32)	-C(33)	-C(34)	175.2(6)
C(37)	-C(32)	-C(33)	-C(34)	-0.4(10)
C(31)	-C(32)	-C(37)	-C(36)	-175.0(7)
C(33)	-C(32)	-C(37)	-C(36)	0.7(11)
C(32)	-C(33)	-C(34)	-C(35)	1.3(11)
C(33)	-C(34)	-C(35)	-C(36)	-2.5(11)
C(34)	-C(35)	-C(36)	-C(37)	2.7(11)
C(35)	-C(36)	-C(37)	-C(32)	-1.8(12)

The sign of the torsion angle is positive if when looking from atom-2 to atom-3 a clockwise motion of atom-1 would superimpose it on atom-4.

The sign of the torsion angle is positive if when looking from atom-2 to atom-3 a clockwise motion of atom-1 would superimpose it on atom-4.


C35
C34
C36
C33
C37
C3
C1
C12
C32
C14
N
C4
C2
C31
C5
C11
C13
C15
C6
C7
C10
C23
C22
C9
Zr
C21
C16
C20
C17
C8
C19
C18
C24
C26
C25
C30
C27
C28
C29


C35
C34
C36
C33
C37
C3
C4
C2
C1
C32
C12
C14
C13
C15
C6
C5
C10
N
C31
C16
C11
C21
C17
C9
C23
Zr
C22
C7
C8
C18
C20
C19
C26
C25
C24
C30
C27
C29
C28